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ON POLARISED ELECTRONIC SPECTRUM OF SINGLE CRYSTAL OF PARADIBROMOBENZENE AT −180°C*

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Plate V

ABSTRACT. The polarisation of the ultraviolet absorption spectra of very thin single crystals of paradibromobenzene at −180°C has been studied by photographing simultaneously the two components with the light vector parallel to *b*- and *c*-axes respectively. It has been observed that although the bands due to $0 \rightarrow v$ transitions are sharp in both the components, the 0, 0 band is sharp only in the *c*-axis spectrum, but in the *b*-axis spectrum it has a triplet structure. The two new bands adjacent to the central 0, 0 band have been assigned to an intermolecular vibration of frequency about 48 cm^{-1} which is coupled to the electronic transition only in the *b*-axis spectrum.

The intensity ratio of the *b*-axis and *c*-axis spectra calculated from the crystallographic data given by Croatto *et al* on the assumption that the transition is a short-axis one, agrees with the observed value. Hence the orientations of the molecules in the lattice as given by Croatto *et al* are correct. The expected Davydov-splitting has been calculated and found to be 15 cm^{-1}, but the poor dispersion of the spectrograph used did not allow the detection of such a small splitting.

INTRODUCTION

The polarised electronic spectrum of single crystal of paradichlorobenzene was recently studied by Sirkar and Misra (1959) and the nature of the spectrum was found to be different from that observed by Craig and Hobbins (1955) in the case of anthracene. It was observed that absorption is much stronger when the light vector is along the *b*-axis of the crystal than that observed with the light vector parallel to the *c*-axis of the crystal. An intermolecular vibration of frequency 53 cm^{-1} is found to be coupled with the 0,0 band in the former spectrum, hereinafter called the *b*-axis spectrum, but no such coupling takes place when the light vector is almost perpendicular to the molecular plane in the latter spectrum. It was further observed that some $0 \rightarrow v$ transitions observed in vapour are absent in the *c*-axis spectrum but they are present in the *b*-axis spectrum. It was also pointed out that the splitting of the two components calculated on

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Davydov's theory (1948) was found to be 22 cm^{-1}, but such a splitting could not be observed.

The crystal of paradibromobenzene belongs to the monoclinic system with two molecules per unit cell and according to Croatto *et al* (1954) it has a structure identical with that of paradichlorobenzene. Also, the crystal structure remains unchanged at −180°C (Krishnamurti, 1959, unpublished work.). So in this case also splitting on Davydov's theory could be easily calculated and verified experimentally.

The study of polarised spectrum of single crystal of paradibromobenzene would be helpful in ascertaining the orientation of the molecules in the lattice and also in finding out the influence of intermolecular forces on the electronic transitions in molecules fixed in crystal lattice. So, the study of polarised electronic spectra of single crystals of *p*-dibromobenzene was undertaken and the results are discussed in this paper.

EXPERIMENTAL

Very thin single crystals of *p*-dibromobenzene were prepared from solution in distilled acetone at room temperature. Larger surface area of the crystallizing basin and very slow rate of evaporation gave crystals of larger size. X-ray rotation photographs were taken for some of the crystals and in all cases, they were found to be developed as thin plates with the *bc*-plane elongated along *c*-axis, the *b*-axis lying along the width of the crystal plate. The primitive translation along *c*-axis was found to be 4.11Å. According to Croatto *et al* (1949) the long axis of the molecule is nearly in the *ab*-plane taking the same general direction as the *a*-axis. The plane of the molecule is tilted with respect to the axial planes to a degree that gives the usual intermolecular separations. The experimental set up was the same as used in an earlier investigation (Sirkar and Misra, 1959). The crystal was mounted with its *c*-axis vertical and the *bc*-face normal to the incident light between two fused silica discs in a brass frame the lower portion of which was immersed in liquid oxygen contained in a Dewar vessel of fused silica.

Spectrograms were taken on Ilford HP3 films with Hilger E1 quartz spectrograph having a dispersion 3Å per mm in the region 2600Å.

Microphotometric records of the spectra were taken with a Kipp and Zonen type self-recording microphotometer. The wavelength of the bands were measured by the method discussed in the earlier paper (Sirkar and Misra, 1959). The disperison in the record was about 2Å or 24 cm^{-1} per mm in the region 2800Å.

RESULTS

Assignment of bands :

The vertical and the horizontal components of the polarised electronic absorption spectrum of *p*-dibromobenzene are reproduced in figure 1 and the

microphotometric records of the bands are shown in figure 2, Plate V. The frequencies of the bands in the two components and their intensities are given in Table I.

The frequencies of the bands due to vapour reported by earlier workers are also included in the table.

TABLE I

Polarised absorption bands of *p*-dibromobenzene at −180°C

Vapour (Sreerama-murty, 1951)		Light vector parallel to *c*-axis		Light vector parallel to *b*-axis	
ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment	ν in cm^{-1}	Assignment
				35391 w	ν_0-48
35643 s	0, 0 (ν_0)	35438 vs	0, 0 (ν_0)	35438 vs	0, 0 (ν_0)
				35485 w	ν_0+47
				35639 m	ν_0+201
		35768 m	ν_0+330	35770 ms	ν_0+332
36113 ms	ν_0+470				
		36022 ms	ν_0+584	36024 ms	ν_0+586
36320 ms	ν_0+677				
		36157 m	ν_0+719	36158 ms	ν_0+720
36657 m	ν_0+1014	36458 s	ν_0+1020	36458 m	ν_0+1020
36787 w	$\nu_0+677+470$	36679 m	ν_0+1241	36679 m	ν_0+1241
37071 m	$\nu_0+1449-21$	36922 m	ν_0+1484		
37092 m	ν_0+1449	37039 w	$\nu_0+1020+581$		
		37177 w	$\nu_0+1020+719$		
37660 w	$\nu_0+2\times1014$	37478 s	$\nu_0+2\times1020$		
37761 vw	$\nu_0+1449+677$	37700 m	$\nu_0+1020+1242$		
38106 w	$\nu_0+1449+1014$	37942 ms	$\nu_0+1020+1484$		
38299 vw	$\nu_0+1449+1014+200$	38500 s	$\nu_0+3\times1020$		
		38959 m	$\nu_0+2\times1019+1483$		

It can be seen from figure 2(*b*) that the 0, 0 band in the horizontal component is broad, but it is sharp in the vertical component; the $0\rightarrow v$ transitions are sharp in both the components.

It is seen from Table I that the bands in two components are approximately in the same position and there is no appreciable shift of any of the components.

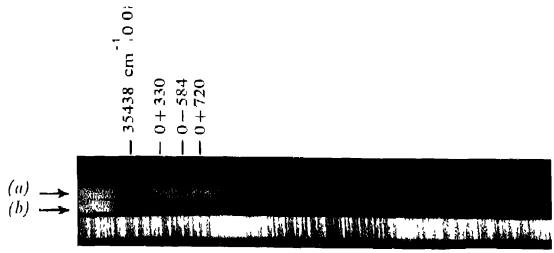

Fig 1 Polarised electronic spectrum of single crysal of *p*−dibromobenzene at −180 C, with light vector (a) parallel to *c* − axis. (b) parallel to *b*−axis.

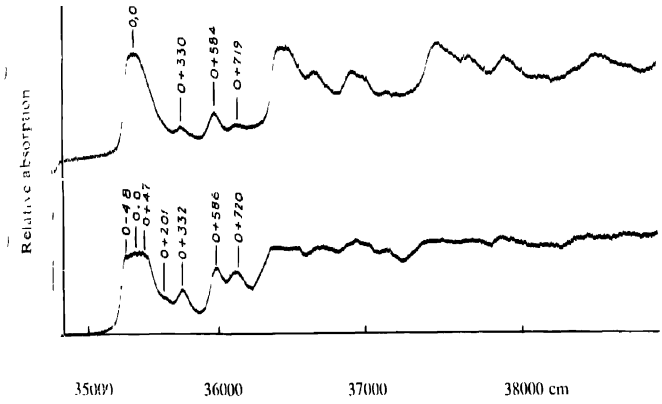

Fig 2 Microphotometric records of the polarised electronic spectrum of single crystal of *p*−dibromobenzene at −180 C
(a) Light vector parallel to *c*−axis *(b)* Light vector parallel to *b* − axis.

DISCUSSION

It can be seen from figure 2(b) that the structure of the 0,0 band is similar to that observed in the case of paradichlorobenzene with light vector parallel to *b*-axis (*b*-axis spectrum). In this component the 0,0 band has a triplet structure, the distance of the two outer components from the central one being 48 cm^{-1}. These two components can be explained on the assumption that they are due to some intermolecular vibration of frequency 48 cm^{-1} which are coupled with the electronic transition when the light vector is along the *b*-axis of the crystal, but no such coupling takes place when the light vector is along the *c*-axis. The other bands in the *b*-axis spectrum are about three times as strong as the corresponding bands in the *c*-axis spectrum. These bands can be attributed to excited state frequencies 201 cm^{-1}, 332 cm^{-1}, 586 cm^{-1}, 720 cm^{-1}, 1020 cm^{-1}, 1241 cm^{-1} and 1484 cm^{-1} respectively. It was pointed out earlier (Sirkar and Misra, 1959) that this intermolecular vibration is coupled to the electronic transition only when the light vector is almost parallel to the plane of the molecule. So, in the present case also the light vector should be nearly parallel to the molecule when it is parallel to the *b*-axis of the crystal. According to the data reported by Croatto *et al* (1949) the molecular plane is almost parallel to the *ab*-plane. Hence the results of present investigation corroborate the data reported by Croatto *et al* (1949). Incidentally, it may be pointed out here that the study of the polarised electronic spectra is helpful in finding out the orientation of the benzene ring in the crystals of substituted benzenes.

The excited state frequencies 201 cm^{-1}, 330 cm^{-1}, 584 cm^{-1} and 720 cm^{-1} were not observed in the spectrum due to the vapour by Sreeramamurty (1951), but he observed two frequencies 470 cm^{-1} and 677 cm^{-1} in this region. These frequencies do not agree with any of the frequencies mentioned above but the frequency 470 cm^{-1} is approximately the mean of 332 cm^{-1} and 586 cm^{-1} and the other one of 586 cm^{-1} and 720 cm^{-1}. If the latter two bands become a little broader in the spectrum due to the vapour they can merge into one another to form a broad band of mean frequency, but the absence of the band 332 cm^{-1} in the spectrum due to the vapour is difficult to understand.

In the case of paradibromobenzene all the $0 \rightarrow v$ transitions in the *b*-axis spectrum are also present in the *c*-axis spectrum although with much smaller intensity. In the case of paradichlorobenzene, however, some of the bands absent in the vertical component appear in the horizontal component, *i.e.*, when the light vector is almost parallel to the short axis of the molecules (Sirkar and Misra, 1959).

According to Croatto *et al* (1952) paradichlorobenzene and paradibromobenzene are isostructural, but the orientations of the molecules with respect to the crystallographic, axes are slightly different in the two cases. Attempts have been made to find out whether the difference in the relative intensities of the two

components of the spectra due to the two crystals is accounted for by this difference in orientation. It was assumed by Sponer (1942) that the electronic transition giving this band system is a short-axis one. The intensity ratios of the *b*-axis and the *c*-axis spectrum were calculated from the crystallographic data of Croatto *et al* (1949) for a short axis transition and it was found to be 3 : 1 for paradibromobenzene and 6 : 1 for paradichlorobenzene. The intensity ratio of the *b*-axis spectrum and *c*-axis spectrum for *p*-dibromobenzene as reproduced in figures 1 and 2 and for *p*-dichlorobenzene as in the previous paper (Sirkar and Misra, 1959) are qualitatively in good agreement with the calculated ratio and Sponer's assignment is shown to be correct.

The agreement between the calculated and the observed intensity ratios for the two spectra supports the crystal structure of the substances and the molecular orientation in the lattice as given by Croatto *et al* (1952).

Davydov Spliting

Using the atomic parameters in the *p*-dibromobenzene crystal lattice given by Croatto *et al* (1949), the angles made by the short and long axes of the molecules with the three crystallographic axes are found to be 62°11′, 49°24′ and 68° for the short axis and 35°48′, 125°45′ and 109°40′ for the long axis respectively and the values of $A/|M|^2$, $B/|M|^2$, $C/|M|^2$ (A, B, C having significances as before) were found out from the relation

$$I_{lk}/|M|^2 = -\frac{e^2}{(r_{lk})^3}\left[2\cos\theta_{l1}\cos\theta_{k1} - \cos\theta_{l2}\cos\theta_{k2} - \cos\theta_{l3}\cos\theta_{k3}\right]$$

where M is the molecular transition moment in Å unit and r_{lk} is the distance between the centres of the two molecules, θ_{l1}, θ_{l2}, θ_{l3} are the angles made by the transition moment of the lth molecule with a set of rectangular axes erected at its centre; θ_{l1} refers to an axis along the line of the centre of the lth and kth molecule. The values of A, B and C for *p*-dibromobenzene are given in Table II.

TABLE II

Neighbour intermolecular integrals for crystalline *p*-dibromobenzene.

Integral	Long axis transition cm^{-1} Å^{-2}	Short axis transition cm^{-1} Å^{-2}
$A/\|M\|^2$	− 62	+ 22
$B/\|M\|^2$	− 29	−328
$C/\|M\|^2$	−539	−111

The splitting between the b and c components will be $8C$ and for the short axis transition it comes out to be $-888\,|M|^2$ and for long axis transition it will be $-4312\,|M|^2$. The negative sign means that the bands in the b-axis spectrum should be shifted towards red relative to those in the c-axis spectrum.

The value of $|M|^2$ was found from the relation (Sklar, 1942)

$$|M|^2 = \frac{3hf}{8\pi^2 mc\nu}$$

where f, the oscillator strength is given by

$$f = 2.3 \times \frac{nc^2m}{N\pi e^2} \cdot 10^3 \int \epsilon d\nu$$

the notations having usual significances.

The value of $\int \epsilon d\nu$ for the solution of p-dibromobenzene and benzene were reported by Klingstedt (1933). The value of oscillator strength for the migration in the ring in para dibromobenzene molecule was 5.8×10^{-3} and the migrational transition moment $|M|^2$ was calculated and found to be 15.38×10^{-3} Å^{-2}.

Hence the splitting expected from Davydov's theory in this case for short axis transition comes out to be 15 cm^{-1} and for long axis transition this value should be 66 cm^{-1}. As in the case of p-dichlorobenzene this band system is due to short axis transition.

From the spectrogram and the microphotometric record it is seen that there is no appreciable shift of the band in the b-axis spectrum from the corresponding bands in the c-axis spectrum. Hence the splitting of 15 cm^{-1} is not observed probably because the dispersion of the spectrograph is too small to allow detection of such a small splitting.

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